

Benthic Flux of Dissolved Nickel into the Water Column of South San Francisco Bay

By Brent R. Topping, James S. Kuwabara, Francis Parchaso, Stephen W. Hager, Andrew J. Arnsberg, and Fred Murphy



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Executive Summary

Field and laboratory studies were conducted between April, 1998 and May, 1999 to provide the first direct measurements of the benthic flux of dissolved (0.2-micron filtered) nickel between the bottom sediment and water column at three sites in the southern component of San Francisco Bay (South Bay), California, ([Background, Fig. 1](#)). Dissolved nickel and predominant ligands (represented by dissolved organic carbon, and sulfides) were the solutes of primary interest. Benthic flux (sometimes referred to as internal recycling) represents the transport of dissolved chemical species between the water column and the underlying sediment.

Water-quality managers are often faced with requests to reconsider criteria for contaminant loads to aquatic systems. This is particularly true in San Francisco Bay where contaminants (e.g., nickel and copper) enter the estuarine water column from a wide range of sources (e.g., municipal and industrial discharge, urban and agricultural runoff, weathering processes, and internal remobilization). There have been frequent demands by managers and the general public to quantify the connections between fluxes of contaminants and the health, abundance, and distribution of biological resources (Kuwabara and others, 1999), motivating three decades of sustained progress by the USGS in better understanding San Francisco Bay. One relatively new field of study in San Francisco Bay focuses on a poorly understood, yet potentially predominant, source of contaminants to the bay: internal recycling or benthic flux of biologically reactive trace metals and ligands. This bioavailability and flux of contaminants and nutrients into the water column of San Francisco Bay is affected by chemical (i.e., oxidation-reduction reactions, complexation and repartitioning) and benthic biological processes (Flegal and others, 1991; Kuwabara and others, 1996; Grenz and others, 2000).

Results described herein integrate current project studies with information needs identified by State Water Resources Control Board and local stakeholders to provide initial determinations of dissolved nickel flux from the sediments into the water column of the South Bay. Recent metal-transport modeling studies by Wood and others (1995) clearly indicated the importance of non-point (including benthic) metal sources to South San Francisco Bay, although nickel was not included in that study. Quantifying and understanding the magnitude and variability of these fluxes are critical to the accurate assessment of contaminant sources and loads as well as to the development of process-integrated water-quality models for this estuary.

With a variety of strategies under consideration to determine Total Maximum Daily Loads (TMDL) of contaminants into the South Bay by point sources, the primary question posed in this study was, "Is the magnitude of the benthic flux of dissolved nickel into South Bay significant

relative to known surface-water inputs?” The question was motivated by a number of factors. First, serpentine formations near the South Bay provide a natural source of nickel that accumulates in bottom sediments. San Francisco Bay in general, and the South Bay in particular, exhibit elevated nickel concentrations in the bottom sediment (~90 - 110 micrograms per gram; Hornberger and others, 1999; Wellise and others, 1999) relative to average crustal concentrations (58 - 75 micrograms per gram; Verhoogen and others, 1970; Riley and Chester, 1971). One might therefore question whether some fraction of this sediment-associated nickel becomes remobilized for transport to the overlying water.

Second, elevated dissolved nickel concentrations in the South Bay have prompted a reexamination of the dominant sources so that appropriate TMDL strategies can be designed and implemented. Third, changes in oxidizing or reducing (redox) conditions and nutrient availability near the sediment-water interface (e.g., during phytoplankton blooms) can dramatically alter the mobility of metals and ligands associated with the bottom sediment as episodic sources of carbon settle out and accumulate (Thompson and others, 1981). Finally, there is a growing body of evidence from other aquatic systems that benthic flux or internal recycling of contaminants and nutrients is an important process to consider in developing appropriate water-quality models for San Francisco Bay (Berelson and others, 1982; Flegal and others, 1991; Kuwabara and others, 1999). The question is therefore posed to provide clarification of existing conceptual models for contaminant transport within the South Bay.

This report is formatted unconventionally in a pyramid-like structure to effectively serve the diverse group of people that want to access the information in various levels of detail ([Appendix 1](#)). The report enables quick transitions between the initial [summary information](#) (figuratively at the top of the pyramid) and later details of [methods](#) or [results](#) (that is, figuratively towards the base) using hyperlinks to supporting figures and tables, and an electronically linked [Table of Contents](#).

Sampling was performed at three U.S. Geological Survey (USGS) designated stations ([Fig. 1](#)) in the South Bay: numbers 25 (a western shoal station with fine silt/clay-textured bottom sediment), 29A (a main channel station with sediment texture similar to station 25), and 46 (an eastern shoal station with sandy bottom-sediment texture). The stations are located 10.3, 1.4 and 2.1 km south of the San Mateo Bridge, respectively (all stations are north of the Dumbarton Bridge). Samples were collected near slack tide before ebb. Therefore, the depths of the shoal stations (25 and 46) were <2 m, and the main-channel station (29A) depth varied between 13 and 14 m. Three replicate sediment cores were collected from two stations for incubation experiments to provide flux estimates and benthic biological characterizations on April 8, 1998, September 16, 1998, and May 26, 1999 ([Fig. 2](#)). Ancillary data, including nutrient and ligand fluxes, were determined to provide a water-quality framework from which to compare the dissolved nickel results. The following major observations from interdependent physical, biological, and chemical data were made:

Physical and Biological Characterizations

1. The surficial sediment at Stations 25 and 29A were of generally higher porosity (range of 0.80 – 0.93; 0.88 ± 0.04) than at Station 46 (range of 0.64 to 0.83; 0.77 ± 0.09), although the difference was not statistically significant at the 95 percent

confidence level ([Table 1](#)). This is consistent with the greater difficulty collecting cores at Station 46 because of the sandier sediment texture than the other two sites.

2. Taxonomic analyses of the macrobenthos indicated highly variable benthic communities over both temporal and spatial scales ([Table 2](#); [Macrobenthos discussion](#)). Macroinvertebrates may enhance the solute flux across the sediment-water interface due to biologically enhance advection (i.e., bioirrigation/ bioturbation as a result of feeding and sensing behaviors).
3. Chlorophyll-*a* concentrations ranged from 0.04 to 13.7 micrograms per square centimeter with highest concentrations observed at Station 25 during the spring, 1998 sampling, and the lowest concentrations at the same site during the fall sampling for that year ([Table 3](#)).
4. Benthic bacterial concentrations were of the order of 10^8 - 10^9 cells per gram-surficial sediment ([Table 4](#)). There are limited reports of bacterial abundances in estuarine sediment, but the observed values are consistent with those found in the Saint Lawrence Estuary ($\sim 10^9$ cells per gram; Lavigne and others, 1997). Microbial communities may be critical in establishing the redox gradients that regulate the remobilization, transformation and subsequent transport of sediment-associated contaminants like nickel. Station 46 consistently exhibited lower bacterial abundance than either Stations 25 or 29A for a given sampling date.

Chemical Characterizations – A summary of observations about measured chemical parameters is provided below. Unless otherwise specified, the concentrations discussed in this section operationally refer to dissolved (i.e., 0.2 micron-filtered samples) concentrations.

1. Water-column concentrations – Dissolved macronutrient concentrations in the bottom water (approximately 1 meter above the sediment-water interface) were consistently higher (frequently by orders of magnitude) than surface-water determinations reported for similar times and locations (Regional Monitoring Program, 2001). This is consistent with measured positive benthic fluxes for the macronutrients ([Table 5](#)).

Dissolved-Ni concentrations in the bottom water over the three sampling dates ranged from a minimum of 34 (Sta. 25, Sept. 1998) to a maximum of 43 nM (Sta. 29A, May 1999). No chemical analyses for surface waters on these dates, at these sites, were available. However, when compared to Regional Monitoring Program data at similar times and locations (Regional Monitoring Program, 2001), higher dissolved-nickel concentrations at depth were only evident during two of the three sampling periods. Dissolved-nutrient data for bottom waters was only available for the spring, 1999 experiment, and indicated bottom-water concentrations that were orders of magnitude higher than surface-water concentrations during that period.

2. Benthic flux of nutrients (nitrogen species, orthophosphate) – Similar to dissolved nickel results, benthic flux of macronutrients determined from core incubations were

consistently significant (that is of equivalent or greater order of magnitude) relative to surface-water inputs ([Table 6](#), [Fig. 3](#)).

3. Benthic flux of nickel – Flux estimates from core-incubations, when areally averaged over the South Bay (554 square kilometers; Cheng and Gartner, 1985), were significant in magnitude relative to freshwater point sources (Davis and others, 1991; San Jose/Santa Clara Water Pollution Control Plant, 1999; Davis and others, 2000) ([Table 7](#), [Fig. 4](#); [Nickel discussion](#)). This is consistent with previous determinations for other metals (Flegal and others, 1991; Flegal and others 1996; Kuwabara et al, 1996), and with the potential remobilization of sediment-associated metals that have been ubiquitously distributed in the South Bay (Wellise and others, 1999).

Since the current study indicates that the magnitude of measured benthic fluxes for nickel were significant relative to major fresh water inputs, metal remobilization from the sediment should be considered in establishing future TMDL strategies for the watershed.

BACKGROUND - What is benthic flux and why should it be considered?

Many fundamental processes affect the transport of dissolved chemical species (e.g., nutrients, metals, or ligands) through and within an estuary. A conceptual model of these processes ([Fig. 5](#)) illustrates some physically based processes that have been examined and carefully quantified for several years (e.g., advective transport and point source inputs) (Fisher and others, 1979).

Conversely, there are flux terms in the conceptual model that have received little attention. A prime example is the benthic flux term where no direct measurements for dissolved nickel have been available. Benthic flux (sometimes referred to as internal recycling) represents the transport of dissolved chemical species between the water column and the underlying sediment. Flux of solutes can be either positive (from the sediment into the water column) or negative (from the water column into the sediment). It can vary over multiple temporal and spatial scales.

As a result of physical, chemical, and biological changes in the vertical cross section of the sediment-water interface, geochemical gradients take on a variety of forms that have been previously reported (Kuwabara and others, 2000; [Fig. 6](#)). When the solute concentration above and below the sediment-water interface are equivalent, there is no discernable gradient, and consequently no net transfer of that substance across the interface; **no benthic flux**. In contrast, when solute concentrations in the water column are higher than those in the bottom sediment pore waters, a **negative** benthic flux results whereby the substance moves **into** the sediment. Dissolved oxygen is a typical example of such a solute where microbial respiration can create a sediment demand for oxygen. When concentrations in the water column are lower than those in sediment pore waters, the vertical concentration gradient can physically drive the **release** of dissolved chemical species from the sediment to the overlying water; a positive benthic flux. The remobilization or chemical transformation of sediment-associated trace metals or ligands may represent such gradients.

The examples above are highly simplified. When interdependent factors regulate the benthic flux of biologically reactive substances, the vertical gradient for one dissolved species may be dependent on the gradient of another chemical species. For example, an **attenuated release** may occur when solute concentrations increase below the sediment-water interface only when another solute is depleted. Dissolved iron often behaves in this manner when suboxic conditions reduce it from ferric to ferrous forms, increasing its solubility. Additionally, macroinvertebrates can biologically enhance the benthic flux by irrigating, or perturbing surficial sediment layers (**bioirrigation**, **bioturbation**, or biologically enhanced **advection**). Certain productive benthic communities can enhance benthic flux beyond diffusive-control estimates by orders of magnitude (Kuwabara and others, 1999). In summary, vertical chemical gradients generated by a variety of interdependent biogeochemical processes induce the movement of a dissolved chemical species like nickel across the sediment-water interface.

Scientists and water-quality managers are only beginning to appreciate the importance of benthic flux in many aquatic environments. In recent years (that is within the past decade or two), researchers have gradually realized that there are non-hydrologic processes (e.g., benthic flux) that must be incorporated into water-quality models to generate physically meaningful modeling results. The USGS has been involved in studies of San Francisco Bay for

approximately three decades, but as with many other disciplines, benthic-flux studies only developed within the past decade (Flegal and others, 1991; Kuwabara and others, 1996). One possible explanation for the lag in these studies relative to other transport processes is the fact that quantifying benthic flux is instrument and manpower intensive. Each flux estimate requires a concentration time series or vertical profile.

As described in the Executive Summary, the primary question posed in this study was, “Is the magnitude of the benthic flux of dissolved nickel significant relative to surface-water inputs?” Although the technical rationale for posing that question is multifaceted ([introductory comments](#)), a major objective of the study was to offer some help and scientific basis for directing TMDL strategies for the watershed by providing the first comparisons of direct benthic-flux measurements to surface water inputs.

RESULTS AND DISCUSSION

Physical Data – There was a visible difference in sediment texture between eastern-shallow Station 46 (sandy; difficult to retain sediment cores), and both the western-shallow Station 25 and the main-channel Station 29A (noticeably higher fraction of silt and clay that facilitated core-tube penetration, and retention of sediment cores). Measured porosities were consistent with that observation and Stations 25 and 29A had higher porosities (0.80 – 0.93) than Station 46 (0.64 to 0.83; [Table 1](#)).

Biological Data

1. Chlorophyll-*a* – Please refer directly to table summaries ([Table 3](#)).
2. Benthic bacteria – The benthic microbial community establishes redox gradients and thereby facilitates changes in the chemical structure, mobility, and biological availability of contaminants. The highest bacterial abundance was observed at Station 25 during April 1998 and was coincident with the highest sulfide fluxes for the study. This suggests an increase in sulfate-reducing bacteria with a source of organic carbon near the sediment-water interface, possibly as a consequence of the spring algal bloom. A similar range of benthic bacterial abundance (of the order of 10^9 cells per gram) was reported for the trough of the Saint Lawrence Estuary (Lavigne and others, 1997).
3. Benthic macroinvertebrates - At Station 46, the eastern shallow station, the dominant taxa in the benthic community changed from annelids in the spring of 1998 to bivalves in the spring of 1999 ([Fig. 7a](#)). The number of taxa, as well as the number of individuals, in the benthic community was greater in 1999 than in 1998. Combined wet weight data also reflected these trends. Annelids represented 89% of total macroinvertebrate biomass in April 1998. In contrast, mollusks represented 69% of total macroinvertebrate biomass in May 1999. However, total biomass was about five times greater in 1999 than in 1998, and annelid biomass in 1999 was greater than 1998.

At Station 25, the western shallow station, the abundance of individuals and the number of taxa were greater in September 1998 than April 1998 ([Fig 7b](#)). In April 1998, many of the common species found in South San Francisco Bay were present. In September 1998 the community was dominated by the filter feeders *Corophium* sp. and *Ampelisca abdita*. Biomass data reflected the equal contribution of crustaceans and annelids to the community in April 1998 and the increase in *Corophium* and *Ampelisca* in September 1998. *Corophium* and *Ampelisca* have been shown to enhance solute benthic flux by their feeding and sensing behaviors (Miller, 1984; Word, 1980). The increase in bivalve biomass between September and April was attributed to the increase in abundance of *Tapes japonica* in September.

Cores from Station 29A, the main channel station, were only obtained in May 1999, and the community composition and biomass was dominated by *Ampelisca abdita* ([Fig. 7c](#)).

Chemical Data – For consistency with previous geochemical studies, flux estimates are provided in molar units.

1. Bottom-water nickel concentrations – In two instances at Station 25 (spring and summer, 1998), the bottom-water concentrations (34 and 43 nanomoles per liter) indicated slightly higher concentrations relative to surface-water concentrations that were determined as part of the Regional Monitoring Program (30 and 35 nanomoles per liter, respectively) ([Table 5](#)). In contrast, the bottom-water concentration at Station 29A in May, 1999 (28 nanomoles per liter) was lower than surface-water determinations at spatially comparable sites (32 and 102 nanomoles per liter at San Bruno Shoals and Redwood Creek, respectively) in April, 1999, the closest RMP sampling date to our experiment.
2. Nickel benthic flux - The magnitude of the benthic flux for dissolved nickel displayed both small scale (within site) and large scale (between site) variability, but were consistently significant, when areally averaged (42 +/- 16 kilograms per day; [Table 7](#)), relative to municipal inputs (3 kilograms per day; San Jose/Santa Clara Water Pollution Control Plant, 1999). Previously, nickel loading to the South Bay from municipal and industrial effluents was estimated at 16 kilograms per day (Davis and others, 1991). Recent estimates by Davis and others (2000) indicate that total nickel loading to San Francisco Bay from external sources is dominated by stormwater runoff. The authors included five hydrologic units (areas) that flow into the South Bay: Alameda Creek, Fremont Bayside, Coyote Creek, Guadalupe River and Palo Alto. Two other hydrologic units, East Bay Cities and San Mateo Bayside, may partially contribute to South Bay inputs. The nickel loading associated with stormwater runoff from all seven units is approximately 56 kilograms per day.

Given ongoing nickel and copper toxicological studies in the South Bay and other parts of the estuary, it may be useful to note that the average dissolved-copper fluxes for stations 25, 29A, and 46 were 7, -1 and -23 nanomoles per square meter per hour, considerably lower than observed nickel fluxes, and distinct because of variable direction.

3. Nutrients - The benthic flux of macronutrients determined in these experiments are comparable to measurements made in 1996, (Grenz and others, 2000), but are considerably lower than measurements made between 1991 and 1993 (Caffrey and others, 1996). This trend is consistent with long-term reductions in phosphorus loading to the South Bay (Schemel and others, 1999). Although the results of this study only provide initial estimates of spatial and temporal variability of these fluxes, measurements reported in this and previous studies suggest that internal recycling of

nutrients in the South Bay needs to be considered when developing models that affect water-quality management decisions for the South Bay.

Because orthophosphate has a high affinity to adsorb onto metal-oxide surfaces under oxic, pH-neutral conditions (Kuwabara, 1992), molar nitrogen to phosphorus (N to P) flux ratios for the South Bay may have particular significance. The molar N to P flux ratios for Stations 29A and 46 in May, 1999, the only date among the three when nutrient concentrations are available, are 19 and 26, respectively ([Fig. 8](#)). By comparison, the molar N to P Redfield Ratio is only 16 (7 by mass ratio; Redfield and others, 1963). That is, on average, approximately 16 moles of nitrogen (220 grams) are taken up for every mole of phosphorus (31 grams) to generate tissue of primary producers. Consistent with other aquatic systems (Kuwabara and others, 2000), the N to P ratios determined for both sites suggest that the sediments can promote the recycling of nitrogen while retarding sediment sources of biogenically derived phosphorus into the water column by sorption/desorption reactions. In contrast, the average molar N to P loading ratio in 1998 for the San Jose/Santa Clara Water Pollution Control Plant was approximately 5 (San Jose/Santa Clara Water Pollution Control Plant, 1999), considerably below the Redfield Ratio. This suggests that surface-water inputs may act as a source of phosphorous for primary production in the South Bay.

Time series of dissolved nutrients from incubated cores indicate that concentration increases in the overlying water primarily occurred in the initial hours of the incubation. The strong initial flux followed by diminished changes in the overlying water chemistry may be due to a shift in the pore-water/bottom-water concentration gradient during the incubation (i.e., that a chemical equilibrium between the pore water and overlying water in certain cores was reached rapidly relative to the entire period of incubation.) This phenomenon occurred with more frequency at Station 46 and is consistent with the lower bottom-water concentrations there relative to the other two sites. Such nonlinearities generated lower flux estimates and coefficients of determination when data from the entire incubation were used in the flux determination as opposed to just to the initial hours ([Table 8](#)). However, even if data over the entire incubation are used in the flux calculation, the areally averaged benthic flux of orthophosphate and nitrogen species are still significant relative to municipal point source inputs ([Table 6](#)). For example, the areally averaged orthophosphate fluxes from Stations 29A and 46 cores were 1,440 and 2,470 kilograms per day, respectively, compared with a freshwater loading of approximately 1,960 kilograms per day, primarily from a major freshwater point source (San Jose/Santa Clara Water Pollution Control Plant, 1999; [Table 6](#), [Fig. 3](#)). Ammonia benthic flux averaged approximately 6,460 and 13,330 kilograms per day from Stations 29A and 46, respectively, compared to only 490 kilograms per day from the same point source.

4. Dissolved organic carbon (DOC) - DOC concentrations serve as a model for the abundance of organic ligands that can complex and enhance the solubility of metals. Certain dissolved metals, in particular nickel, predominantly exist as organic complexes in many aquatic systems (Mantoura and others, 1978; McKnight and

others, 1983, Donat and others, 1994). The benthic flux of DOC exhibited both small-scale (within-site) and large-scale (between-site) variability, ranging from – 239 to 676 micromoles per square meter per hour ([Table 9](#)).

Bottom-water DOC concentrations were highest in summer 1998 (St. 25, 341 micromoles per liter) and lowest in spring 1999 (St. 29A, 141 micromoles per liter). When compared with RMP surface-water data, bottom-water DOC concentrations showed a vertical gradient (higher concentration at depth) in only two of three sites, similar to nickel. In contrast to many of the dissolved inorganic substances, DOC benthic fluxes did not exhibit consistent trends.

5. Dissolved Sulfides – Dissolved sulfides represent a metastable ligand with high affinity to complex most divalent metals like nickel (Hogfeldt, 1983). Sulfide flux was consistently positive (that is, from the sediment to the overlying water column) and ranged from 181 to 752 nanomoles per square meter per day. The highest sulfide fluxes were observed in April 1998, and were significantly higher than the other two dates ([Table 10](#)). Notably, the highest bacterial abundances also were observed during that sampling event.

STUDY DESIGN AND METHODS

The protocol described in this section focuses on method applications in this series of three core-incubation experiments. Details (e.g., quality control specifications) for each analysis has been previously documented (Woods and others, 1999).

Coring Operation

On each of three sampling days (4/8/98, 9/16/98, 5/26/99), four cores were collected at each of two sites using a coring device fabricated from non-metallic parts (Saville Corporation, Minnetonka, Minnesota). To avoid sample contamination, wetted surfaces of the coring device and core tubes were acid-washed polypropylene or fluoroethylene polymer. The eight cores were aerated overnight to condition wetted surfaces before the incubation period ([Fig. 2](#), [Fig. 9](#)). Based on visual determination of any disturbances of the sediment-water interface, three of the four cores per site were selected for incubation. No cores were taken 9/16/98 at station 46 due to operator error. Therefore, only four suitable cores, all from station 25, were collected and incubated for this date. Water overlying the sediments in the selected cores was sampled at four intervals during a 12-hour incubation. Trace element and nutrient samples were processed in a Class-100 laminar-flow hood. The concentration time series was used to determine the benthic flux from each of the incubated cores.

Physical Data

Sediment Porosity – After core-incubations, approximately 10 milliliters of surficial sediment was collected from each core, then bottled, and refrigerated in darkness. Wet weight and dry weight after lyophilization was measured to calculate porosity ([Table 1](#)).

Biological Data

1. Benthic Macrofauna – After core incubations, each core was sieved (500-micron mesh). The sieved samples were fixed with 10% buffered formalin, transferred to 70% ethanol, then sorted and identified to the lowest practicable taxonomic level ([Fig. 10](#)).
2. Benthic Chlorophyll-*a* - Each incubated core was sub-sampled in triplicate for benthic chlorophyll-*a*. Surficial sediment was collected on a glass-fiber filter and buffered with magnesium carbonate. Samples were then frozen in darkness until spectrophotometrically analyzed (Thompson and others, 1981; Franson, 1985) ([Fig. 11](#)).

3. Benthic Bacteria - After core incubations, each core was sub-sampled using a syringe corer. Approximately 10 milliliters of surficial sediment was collected and fixed with 0.5 milliliters of 37% formalin. Samples were then refrigerated in darkness. Benthic bacterial concentrations were determined by direct epifluorescent counts using acridine-orange preparations.

Chemical Parameters

1. Bottom-water sampling – Prior to coring at each sampling site, water-column samples were collected for trace metals analyses primarily using inductively coupled plasma mass spectrometry. In May, 1999, samples were also analyzed for dissolved (0.2-micron filtered) macronutrients by automated spectrophotometry. Samples were pumped from approximately 1 meter above the bottom using a high-displacement peristaltic pump and a tethered length of rigid fluoroethylene polymer tubing.
2. Nutrients (nitrogen species and orthophosphate) – Dissolved nutrients from water-column sampling, and core incubations were filtered with 0.2 micron polycarbonate filters. The filtered samples were immediately refrigerated in darkness, but unlike trace metal samples, were not acidified. Nutrient analyses were performed by automated spectrophotometry ([Fig. 12](#)).
3. Dissolved Nickel – Nickel samples from water-column sampling, and core incubations were filtered with 0.2 micron acid-washed polycarbonate filters. Filtered samples were acidified with quartz-distilled nitric acid to 0.03N, and refrigerated in darkness until analyses. Metal analyses were performed by flow-injection inductively coupled plasma mass spectrometry (FIAS ICP-MS) using external standardization ([Fig. 13](#)).
4. Dissolved organic carbon (DOC) – Dissolved organic carbon was determined by high-temperature non-catalytic combustion (Qian and Mopper, 1997). Potassium phthalate was used as the standard. Low-DOC water (blanks <40 micrograms-organic C per liter) was generated from a double-deionization unit with additional ultraviolet treatment (Milli-Q Gradient – Millipore Corporation) ([Fig. 14](#)).
5. Sulfides – Dissolved sulfides in overlying-water samples were analyzed by square-wave voltammetry (Kuwabara and Luther, 1993) ([Fig. 15](#)).

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Product names are provided for identification purposes only and do not constitute endorsement by the U.S. Geological Survey.

Appendix 1: Comments on the Report Structure

A major objective of this electronic document is to provide a structure that is easily accessible to a potentially wide range of interests in this work. Agency reports in the form of electronically linked products are a fairly recent alternative, but pathways within this document have been constructed to be both logical and intuitive. In addition to hyperlinks within the document to supporting figures and tables, Appendices 2 and 3 provide a quick way to directly review and examine all figures and tables.

Although hard copies of this report are available on request, the advantages of the electronic version relative to the hard copy are substantial in many respects, but particularly in speed of information access at multiple levels of detail.

Your comments about how to improve this evolving type of product are most welcome and may be directed to any of the email addresses provided in the title page, but we request that at least a copy of all comments about the report be addressed to the major author (btopping@usgs.gov) so that they may be compiled for future revisions and reports.

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Fig. 1

Benthic-flux Coring Sites

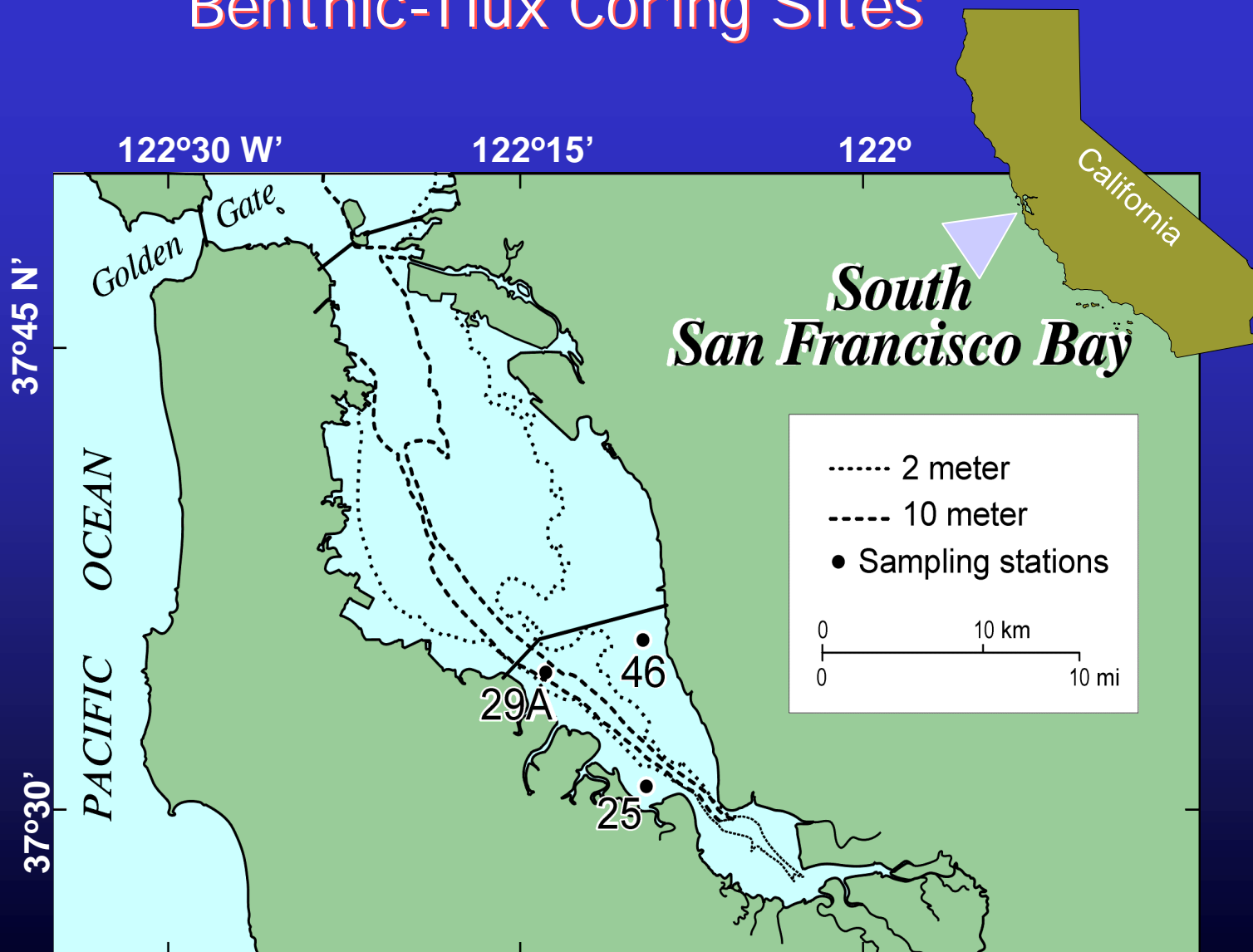
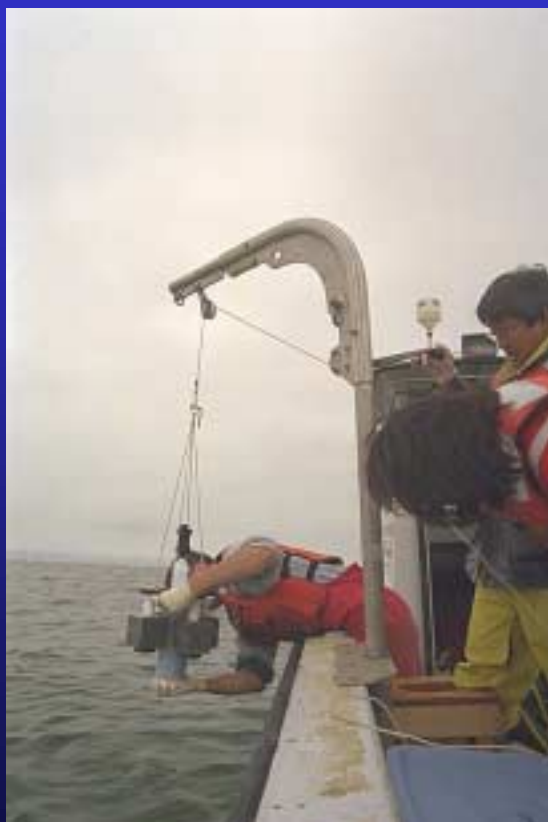


Fig. 2

Coring Operation



Release



Retrieval



Removal

Fig. 3

Nutrient Comparison

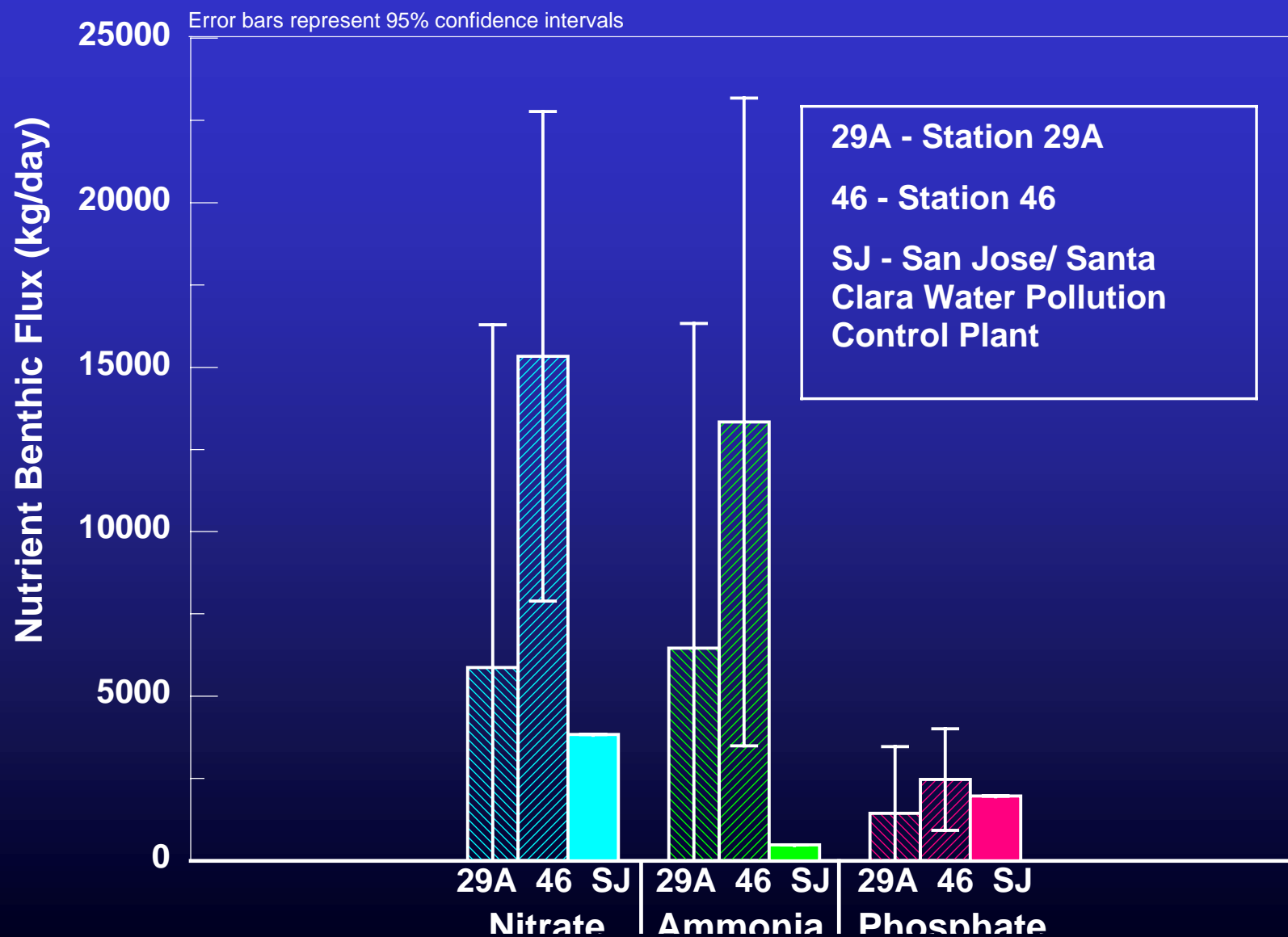


Fig. 4

Nickel Comparison

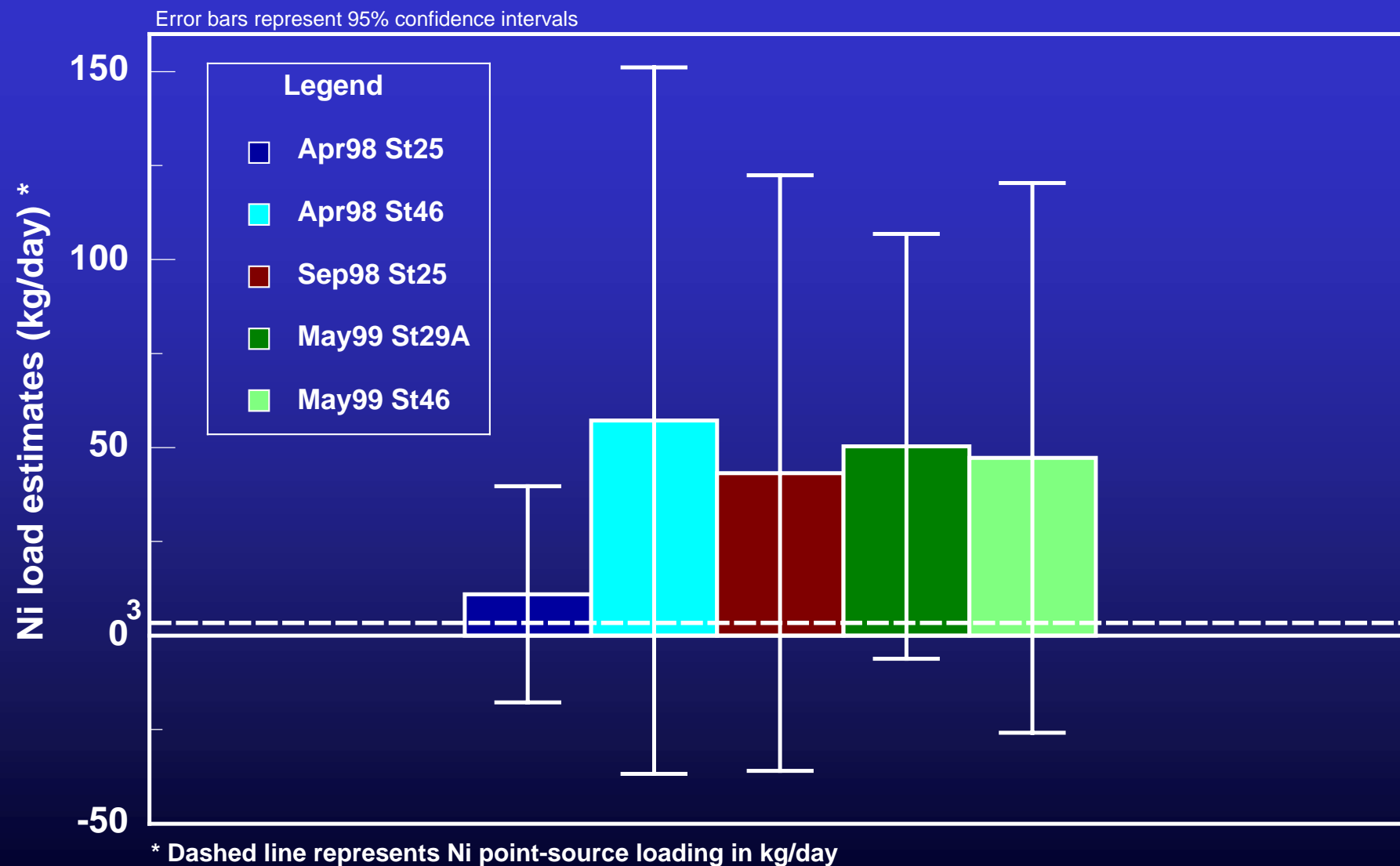


Fig. 5

Conceptual Model of Solute Transport

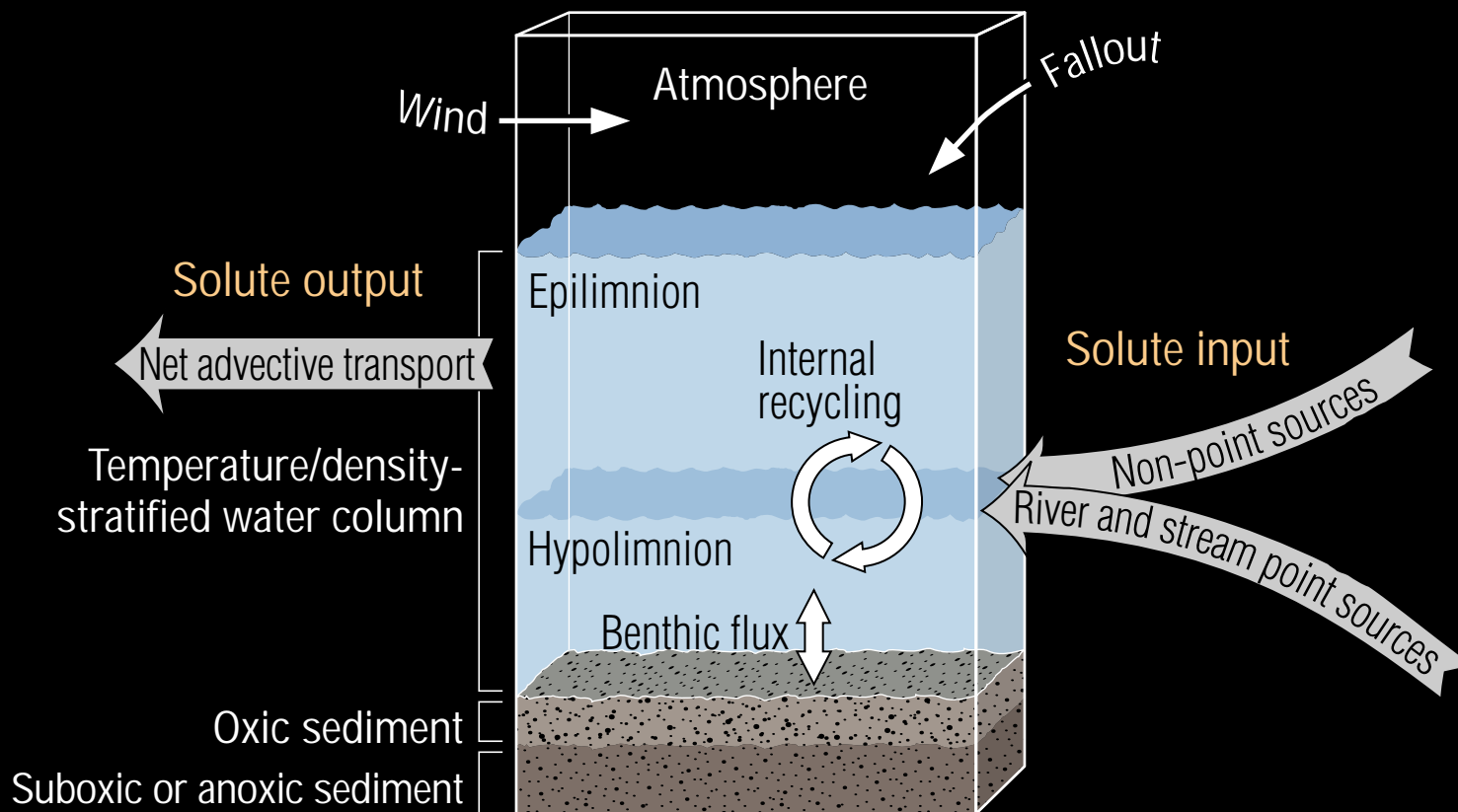


Fig. 6

Processes Regulating Benthic Flux

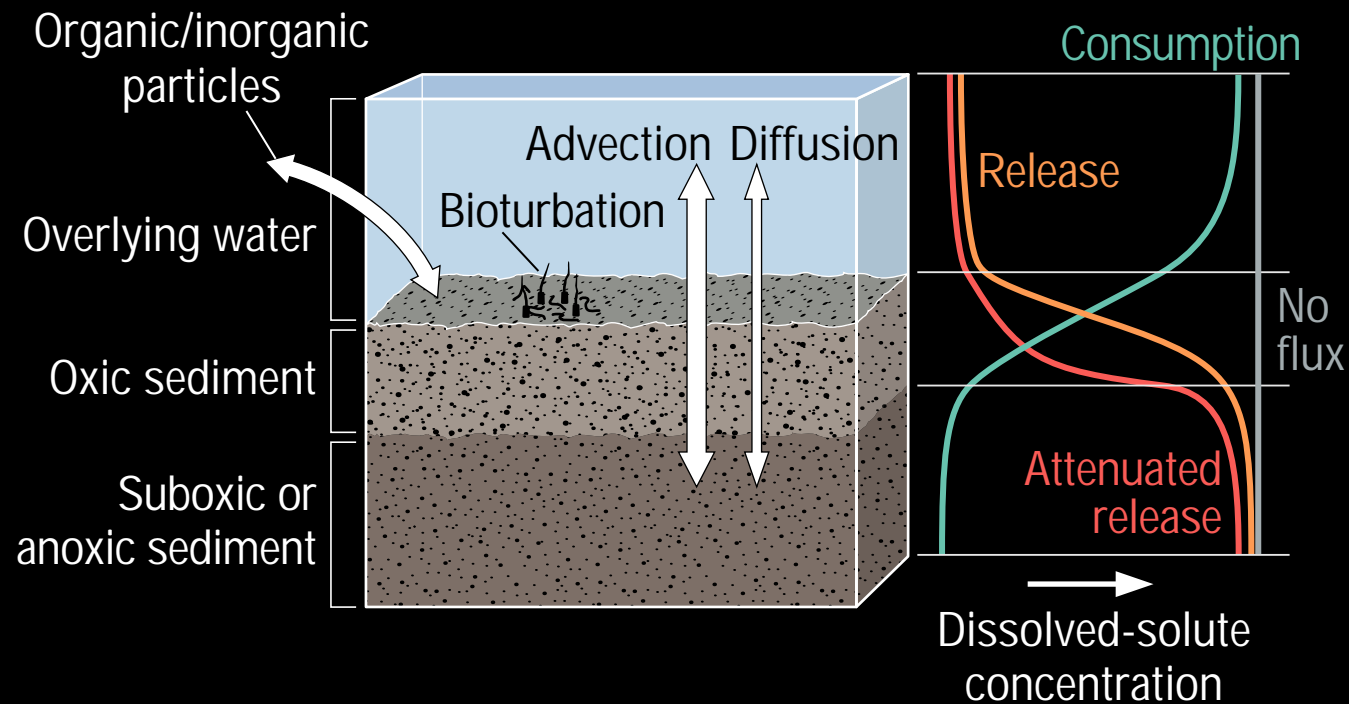


Fig. 7a

Macroinvertebrate Densities at Eastern Shallow Station 46

Note: If there is no bar, the corresponding species was not found in those samples.

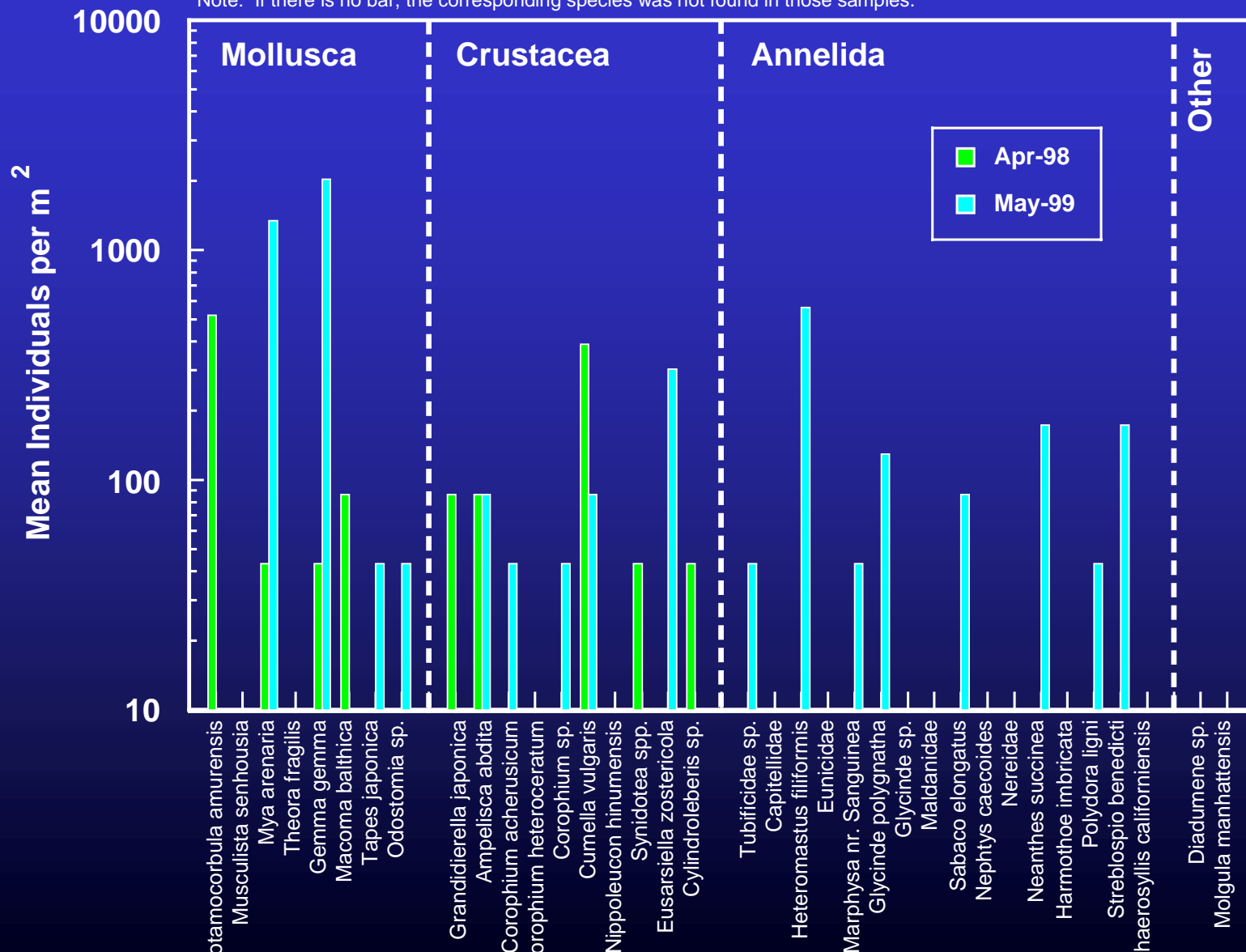


Fig. 7b

Macroinvertebrate Densities at Western Shallow Station 25

Note: If there is no bar, the corresponding species was not found in those samples.

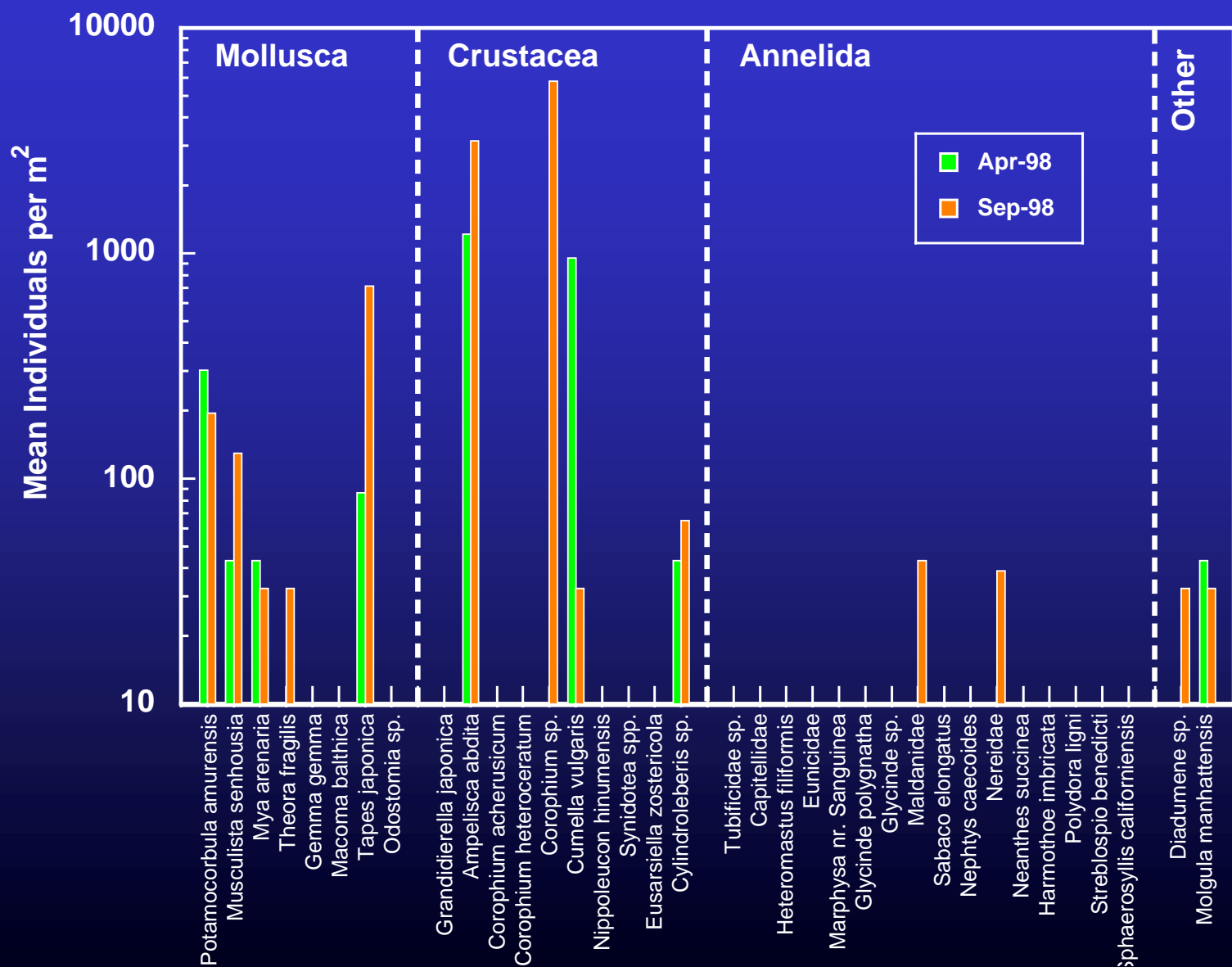


Fig. 7c

Macroinvertebrate Densities at Main Channel Station 29A

Note: If there is no bar, the corresponding species was not found in those samples.

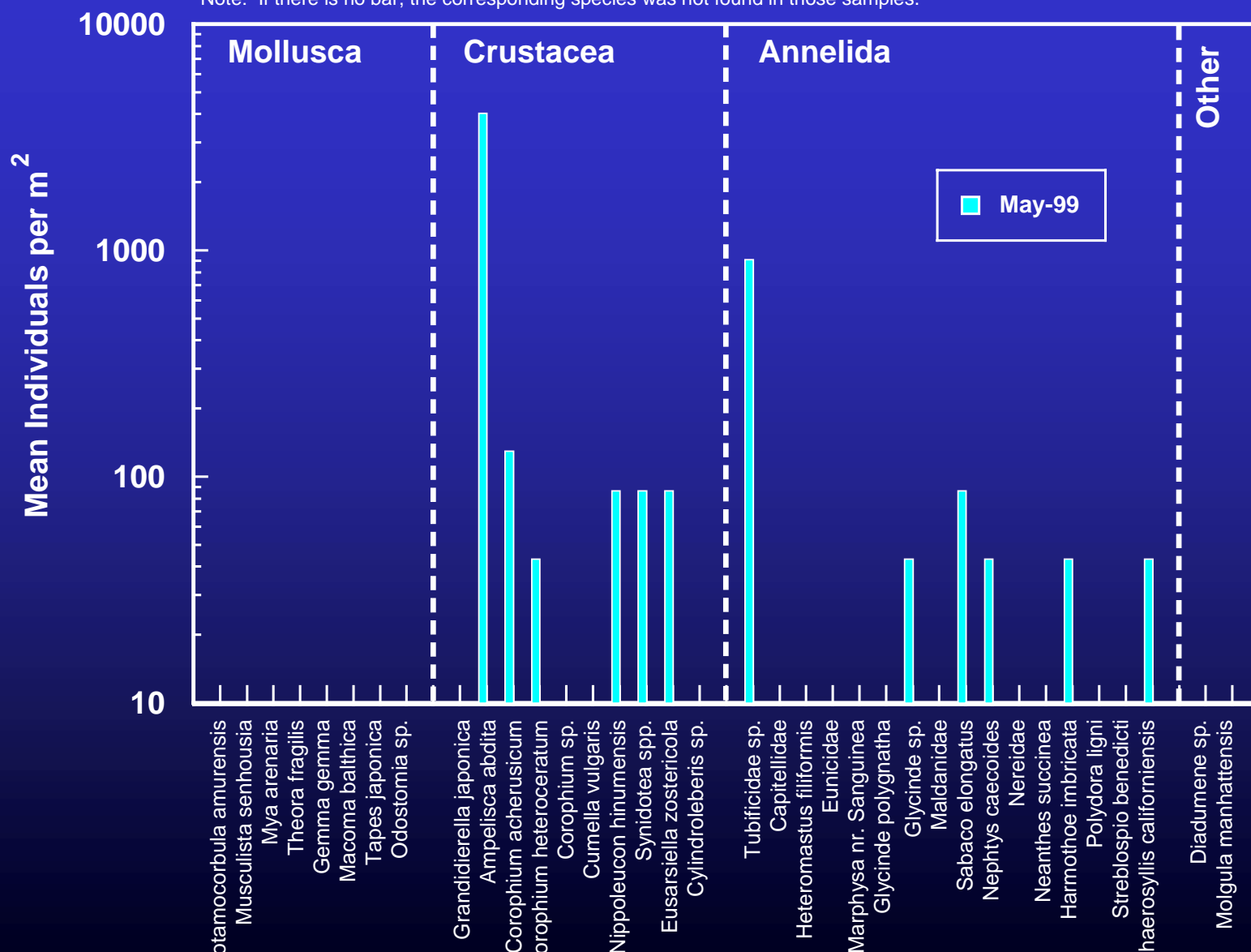


Fig. 8

Nitrogen to Phosphorus Ratio

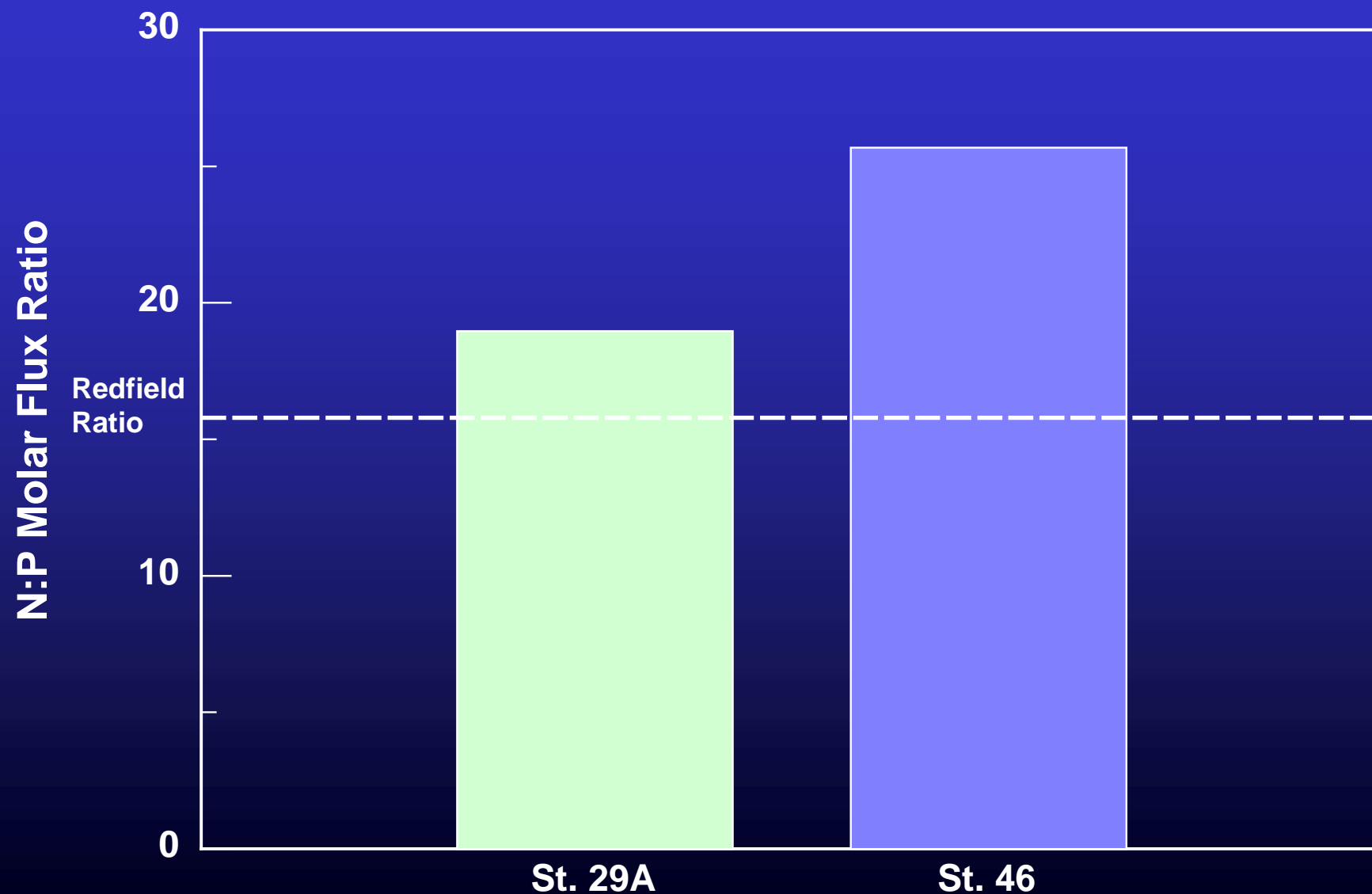


Fig. 9

Incubation Core Design

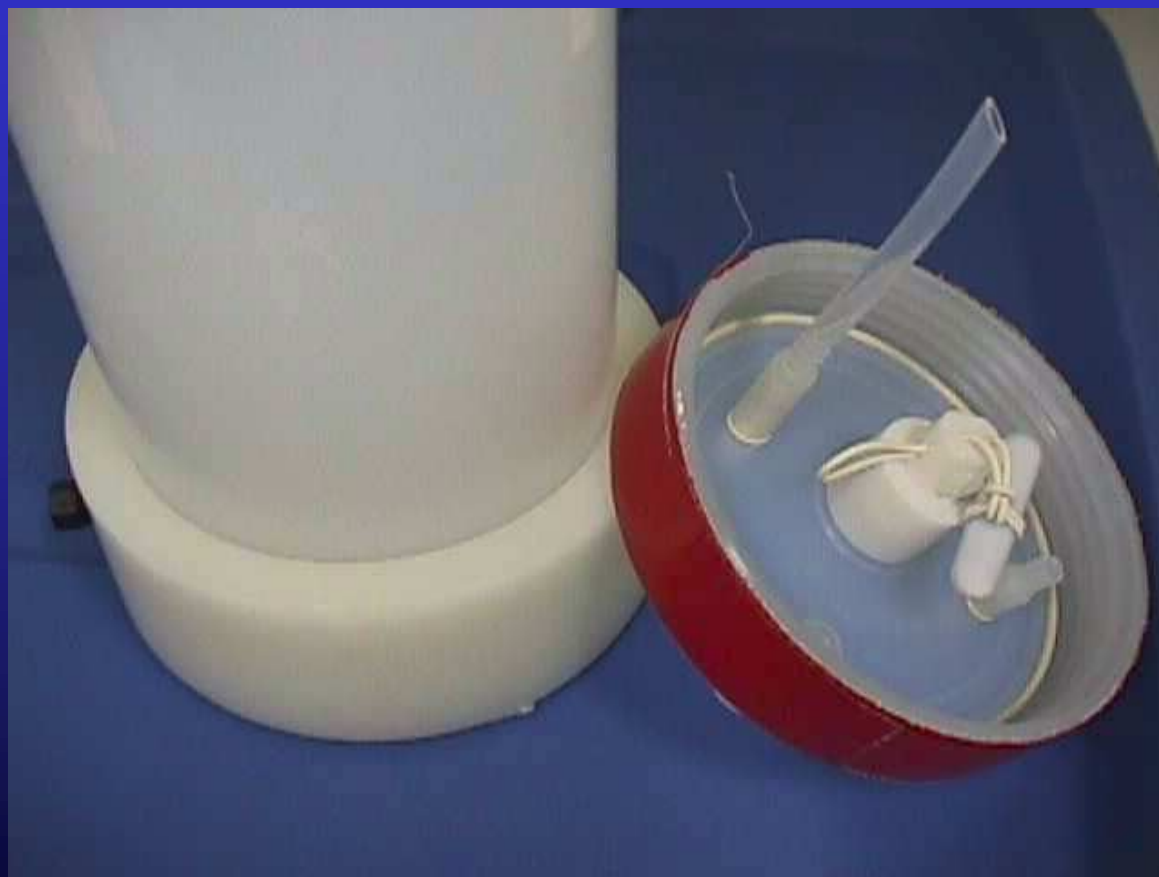


Fig. 10

Benthic Macroinvertebrate Taxonomy



Fig. 11

Benthic Chlorophyll Analyses



Fig. 12

Spectrophotometric Nutrient Analyses



Fig. 13

Dissolved-nickel Analyses by ICP-MS



Fig. 14

Dissolved Organic Carbon (DOC) Analyses by High-Temperature Non-Catalytic Oxidation



Fig. 15



Table 1. Surficial-sediment Porosities

4/8/98				
Station	Core	Porosity	Bulk Density (g-dry/cm ³ -sed)	Wet/dry weight
25	6	0.85	0.33	3.68
25	7	0.92	0.17	6.56
25	8	0.95	0.12	9.38
46	1	0.83	0.38	3.28
46	3	0.81	0.43	2.93
46	4	0.83	0.41	3.11

9/16/98				
Station	Core	Porosity	Bulk Density (g-dry/cm ³ -sed)	Wet/dry weight
25	1	0.93	0.15	7.45
25	2	0.88	0.27	4.39
25	3	0.91	0.20	5.66
25	4	0.87	0.26	4.48

5/26/99				
Station	Core	Porosity	Bulk Density (g-dry/cm ³ -sed)	Wet/dry weight
29A	2	0.80	0.47	4.41
29A	3	0.85	0.37	5.39
29A	4	0.83	0.43	4.79
46	6	0.79	0.48	4.37
46	7	0.73	0.61	3.55
46	8	0.64	0.82	2.97

Table 2. Macrobenthos

Mean number of individuals per square meter based on core surface area of 77 square centimeters.

Note:Species are listed below in the same order as on the plots	Click on station name to see corresponding plot				
	Station: 46		Station: 25		Sta: 29A
	individuals/m ²		individuals/m ²		individ./m ²
	08-Apr-98	25-May-99	08-Apr-98	15-Sep-98	25-May-99
Phylum Mollusca					
Class Bivalvia					
<i>Potamocorbula amurensis</i>	520		303	195	
<i>Musculista senhousia</i>			43	130	
<i>Mya arenaria</i>	43	1342	43	32	
<i>Theora fragilis</i>				32	
<i>Gemma gemma</i>	43	2035			
<i>Macoma balthica</i>	87				
<i>Tapes japonica</i>		43	87	714	
Class Gastropoda					
<i>Odostomia</i> sp.		43			
Phylum Arthropoda					
Class Crustacea					
Order Amphipoda					
Family Gammaridae					
<i>Grandidierella japonica</i>	87				
Family Ampeliscidae					
<i>Ampelisca abdita</i>	87	87	1212	3150	4027
Family Corophidae					
<i>Corophium acherusicum</i>		43			130
<i>Corophium heteroceratum</i>					43
<i>Corophium</i> sp.		43		5813	
Order Cumacea					
<i>Cumella vulgaris</i>	390	87	953	32	
<i>Nippoleucon hinumensis</i>					87
Order Isopoda					
<i>Synidotea</i> spp.	43				87
<i>Eusarsiella zostericola</i>		303			87
Subclass Ostracoda					
<i>Cylindroleberis</i> sp.	43		43	65	
Phylum Annelida					
Class Oligochaeta					
<i>Tubificidae</i> sp.		43			909
Class Polychaeta					
Family Capitellidae					
Capitellidae *	0		0	0	
<i>Heteromastus filiformis</i>		563			
Family Eunicidae					
Eunicidae *				0	
<i>Marphysa</i> nr. <i>Sanguinea</i>		43			
Family Goniatdidae					
<i>Glycinde polygnatha</i>		130			
<i>Glycinde</i> sp.					43
Family Maldanidae					
Maldanidae *	0		0	43	
<i>Sabaco elongatus</i>		87			87
Family Nephtyidae					
<i>Nephtys caecoides</i>					43
Family Nereidae					
Nereidae *	0			39	
<i>Neanthes succinea</i>		173			
Family Polynoidae					
<i>Harmothoe imbricata</i>					43
Family Spionidae					
<i>Polydora ligni</i>		43			
<i>Streblospio benedicti</i>		173			
Family Syllidae					
<i>Sphaerosyllis californiensis</i>					43
Phylum Cnidaria					
<i>Diadumene</i> sp.				32	
Phylum Tunicata					
<i>Molgula manhattensis</i>			43	32	

* Within these rows, zeros represent samples where the presence of worm fragments prevented indentification beyond the family level. These values are thus excluded from quantification.

Combined wet wts. grams	Station: 46		Station: 25		Sta. 29A
	08-Apr-98	25-May-99	08-Apr-98	15-Sep-98	25-May-99
Molluscs	0.021	0.737	0.004	0.672	
Crustaceans	0.002	0.002	0.084	0.021	0.025
Annelids	0.186	0.324	0.049	0.531	0.003
Cnidaria					
Tunicata			0.084	0.063	

Table 3. Discrete Benthic Chlorophyll Analysis

4/8/98		Chlorophyll-a	
		Mean	S.D.
Station	Core	ug/cm ²	ug/cm ²
25	6	2.26	0.11
25	7	10.96	2.35
25	8	6.82	5.39
46	1	2.27	1.52
46	3	3.92	0.28
46	4	2.76	0.78

9/16/98		Chlorophyll-a	
		Mean	S.D.
Station	Core	ug/cm ²	ug/cm ²
25	1	0.27	0.11
25	2	0.60	0.32
25	3	0.04	0.06
25	4	0.62	0.15

5/26/99		Chlorophyll-a	
		Mean	S.D.
Station	Core	ug/cm ²	ug/cm ²
29A	2	0.81	0.34
29A	3	2.55	1.29
29A	4	2.03	1.67
46	6	0.59	0.19
46	7	1.14	0.86
46	8	0.56	0.11

S.D.=Standard deviation

Table 4 Benthic Bacteria Concentrations for Core IncubationsValues in 10^8 bacteria cells per gram of core material

4/8/98		Bacteria concentrations 10^8 cells/g-core			
Station	Core	mean	CI	n	
25	6	20.2	+/- 2.0	48	
25	7	17.3	+/- 2.0	48	
25	8	31.0	+/- 3.5	48	
46	1	15.8	+/- 1.9	48	
46	3	13.9	+/- 1.7	48	
46	4	6.8	+/- 0.8	48	

9/16/98		Bacteria concentrations 10^8 cells/g-core			
Station	Core	mean	CI	n	
25	1	5.6	+/- 0.7	48	
25	2	3.9	+/- 0.3	48	
25	3	4.8	+/- 0.5	48	
25	4	4.1	+/- 0.4	48	

5/26/99		Bacteria concentrations 10^8 cells/g-core			
Station	Core	mean	CI	n	
29A	2	12.5	+/- 0.8	48	
29A	3	10.4	+/- 1.0	48	
29A	4	12.8	+/- 0.9	48	
46	6	5.0	+/- 0.6	48	
46	7	4.1	+/- 0.4	48	
46	8	3.1	+/- 0.4	48	

CI=95% confidence interval

n=number of samples

Table 5 Water Column: Comparison between bottom water and comparable surface water

Nickel		RMP data		Bottom water data		
Sta.		Date	Ni (nM)	Ni (nM)	Date	Sta.
RC	4/22/98	30		34	4/8/98	25
				30	4/8/98	46
RC	7/20/98	35		43	9/16/98	25
RC&SB	4/12/99	67		28	5/26/99	29A
				33	5/26/99	46
Ammonia		RMP data		Bottom water data		
Date		NH4 (mg/L)		NH4 (mg/L)	Date	Sta.
RC	4/22/98	0.02			4/8/98	25
					4/8/98	46
RC	7/20/98	0.03			9/16/98	25
RC&SB	4/12/99	0.04		11.14	5/26/99	29A
				0.93	5/26/99	46
Nitrate		RMP data		Bottom water data		
Date		N03 (mg/L)		N03 (mg/L)	Date	Sta.
RC	1/27/98	0.6				
RC	4/22/98	n/a			4/8/98	25
					4/8/98	46
RC	7/20/98	0.3			9/16/98	25
RC&SB	4/12/99	0.1		23.99	5/26/99	29A
				11.86	5/26/99	46
Nitrite		RMP data		Bottom water data		
Date		N02 (mg/L)		N02 (mg/L)	Date	Sta.
RC	4/22/98	0.037			4/8/98	25
					4/8/98	46
RC	7/20/98	0.012			9/16/98	25
RC&SB	4/12/99	0.004		1.18	5/26/99	29A
				0.18	5/26/99	46
Phosphate		RMP data		Bottom water data		
Date		PO4 (mg/L)		PO4 (mg/L)	Date	Sta.
RC	4/22/98	0.06			4/8/98	25
					4/8/98	46
RC	7/20/98	0.24			9/16/98	25
RC&SB	4/12/99	0.05		3.86	5/26/99	29A
				3.23	5/26/99	46
DOC		RMP data		Bottom water data		
Date		DOC (uM)		DOC (uM)	Date	Sta.
RC	4/22/98	177		263	4/8/98	25
				267	4/8/98	46
RC	7/20/98	221		341	9/16/98	25
RC&SB	4/12/99	167		141	5/26/99	29A
				172	5/26/99	46

RC represents RMP's Redwood Creek site

SB represents RMP's San Bruno site

RC&SB is an average of Redwood Creek and San Bruno values

mg/L=milligrams per liter

uM=micromoles per liter

Table 6 Dissolved Nutrient Flux from Core Incubations on May 26, 1999

Molar N:P Flux Ratios	
St. 29A	19.0
St. 46	25.7

							Flux vs. Load comparison		
Nitrate (NO3) plus Nitrite							Station*	Areally**	City of SJ
Nitrate Flux (umoles/m ² -h)							mean&ci	averaged	NO3 load
Station	Core	Mean	CI		r ²	n	in um/m ² /hr	in kg/day	in kg/day
29A	2	10 +/-	18		0.14	4	32	5873	3831
29A	3	42 +/-	7		0.95	4	+/-	+/-	
29A	4	42 +/-	15		0.79	4	56	10416	
46	6	72 +/-	97 Initial flux dominated		0.22	4	82	15337	3831
46	7	97 +/-	94 Initial flux dominated		0.35	4	+/-	+/-	
46	8	78 +/-	95 Initial flux dominated		0.25	4	40	7439	

Ammonia (NH4)							Station*	Areally**	City of SJ
Ammonia Flux (umoles/m ² -h)							mean&ci	averaged	NH4 load
Station	Core	Mean	CI		r ²	n	in um/m ² /hr	in kg/day	in kg/day
29A	2	15 +/-	38		0.07	4	35	6465	487
29A	3	48 +/-	16		0.81	4	+/-	+/-	
29A	4	41 +/-	29 Initial flux dominated		0.51	4	53	9866	
46	6	64 +/-	90 Initial flux dominated		0.20	4	72	13334	487
46	7	60 +/-	84 Initial flux dominated		0.20	4	+/-	+/-	
46	8	92 +/-	81 Initial flux dominated		0.39	4	53	9844	

Reactive Phosphate (DRP)							Station*	Areally**	City of SJ
DRP Flux (umoles/m ² -h)							mean&ci	averaged	DRP load
Station	Core	Mean	CI		r ²	n	in um/m ² /hr	in kg/day	in kg/day
29A	2	2.3 +/-	1.5		0.54	4	3	1439	1963
29A	3	2.8 +/-	0.8		0.86	4	+/-	+/-	
29A	4	5.3 +/-	1.5		0.86	4	5	2025	
46	6	6.8 +/-	5.3 Initial flux dominated		0.45	4	6	2469	1963
46	7	6.6 +/-	5.9 Initial flux dominated		0.39	4	+/-	+/-	
46	8	4.6 +/-	6.2 Initial flux dominated		0.21	4	4	1540	

Nitrite						
Nitrite Flux (umoles/m ² -h)						
Station	Core	Mean	CI		r ²	n
29A	2	4.0 +/-	3.9 Initial flux dominated		0.34	4
29A	3	12.4 +/-	1.4		0.97	4
29A	4	12.1 +/-	4.0		0.82	4
46	6	5.3 +/-	8.1 Initial flux dominated		0.17	4
46	7	6.0 +/-	8.2 Initial flux dominated		0.21	4
46	8	6.4 +/-	8.1 Initial flux dominated		0.24	4

Inorganic Nitroen (DIN)						
DIN Flux (umoles/m ² -h)						
Station	Core	Mean	CI		r ²	n
29A	2	25 +/-	49		0.12	4
29A	3	90 +/-	20		0.91	4
29A	4	83 +/-	44		0.64	4
46	6	136 +/-	187 Initial flux dominated		0.21	4
46	7	157 +/-	178 Initial flux dominated		0.28	4
46	8	169 +/-	176 Initial flux dominated		0.32	4

Silica						
Silica Flux (umoles/m ² -h)						
Station	Core	Mean	CI		r ²	n
29A	2	233 +/-	69		0.85	4
29A	3	242 +/-	59		0.89	4
29A	4	294 +/-	95		0.83	4
46	6	75 +/-	40 Initial flux dominated		0.64	4
46	7	90 +/-	27		0.85	4
46	8	109 +/-	36		0.82	4

* Mean of the three flux values for the given station, with 95% confidence interval
** Mean values averaged over the South Bay area (554 km2, Cheng and Gartner, 1985)

Table 7 Dissolved Nickel Flux from Core Incubations

							Flux vs. Load comparison		
April, 1998							Station*	Areally**	City of SJ
Ni Flux (nmoles/m ² -h)							mean&ci	averaged	Ni load
Station	Core	Mean	CI	r ²	n		in nM/m ² /hr	in kg/day	in kg/day
25	6	25.9 +/-	4.3	0.48	17		14.0	10.9	3.0
25	7	14.5 +/-	8.4	0.16	12		+/-	+/-	
25	8	1.7 +/-	2.5	0.02	13		36.8	28.8	
46	1	65.1 +/-	7.7	0.72	15		73.3	57.2	3.0
46	3	116.3 +/-	10.5	0.81	15		+/-	+/-	
46	4	38.6 +/-	2.8	0.95	10		120.3	93.9	

September, 1998							Station*	Areally**	City of SJ
Ni Flux (nmoles/m ² -h)							mean&ci	averaged	Ni load
Station	Core	Mean	CI	r ²	n		in nM/m ² /hr	in kg/day	in kg/day
25	1	94.6 +/-	8.3	0.79	16		55.4	43.2	3.0
25	2	32.3 +/-	8.2	0.44	13		+/-	+/-	
25	3	106.3 +/-	19.2	0.61	13		101.5	79.2	
25	4	-11.6 +/-	13.9	0.02	15				

May, 1999							Station*	Areally**	City of SJ
Ni Flux (nmoles/m ² -h)							mean&ci	averaged	Ni load
Station	Core	Mean	CI	r ²	n		in nM/m ² /hr	in kg/day	in kg/day
29A	2	39.9 +/-	7.4	0.60	13		64.5	50.3	3.0
29A	3	66.1 +/-	9.2	0.72	13		+/-	+/-	
29A	4	87.4 +/-	12.4	0.64	15		72.5	56.6	
46	6	53.8 +/-	5.3	0.79	15		60.5	47.2	3.0
46	7	33.7 +/-	4.6	0.70	14		+/-	+/-	
46	8	94.1 +/-	12.1	0.76	13		93.7	73.1	

* Mean of the three (or four) flux values for the given station, with 95% confidence interval

** Mean values averaged over the South Bay area (554 km², Cheng and Gartner, 1985)

CI=95% confidence interval

Average and CI for Ni flux estimates in kg/day			
41.9	+/-	16.4	n=16

Table 8. Comparison of nutrient fluxes using two or twelve hours of incubation data

All dissolved fluxes		
St.46 in $\mu\text{mol}/\text{m}^2/\text{hr}$		
Core	All 12 hrs	First 2 hrs
Nitrite		
6	5	74
7	6	76
8	6	78
Nitrate plus nitrite		
6	72	890
7	97	904
8	78	882
Phosphate		
6	7	53
7	7	57
8	5	58
Silica		
6	75	395
7	90	240
8	109	433
Ammonia		
6	64	836
7	60	789
8	92	807
Inorganic nitrogen		
6	136	1726
7	157	1693
8	169	1690

Table 9. Dissolved Organic Carbon Flux from Core Incubations

April, 1998		DOC Flux (umoles/m ² -h)				
Station	Core	Mean	CI	r ²	n	
25	6	539 +/-	92	0.59	14	
25	7	-32 +/-	38	0.02	18	
25	8	-71 +/-	14	0.42	16	
46	1	676 +/-	160	0.47	13	
46	3	-222 +/-	80	0.24	14	
46	4	89 +/-	17	0.48	15	

September, 1998		DOC Flux (umoles/m ² -h)				
Station	Core	Mean	CI	r ²	n	
25	1	328 +/-	58	0.62	13	
25	2	-68 +/-	55	0.06	14	
25	3	-80 +/-	12	0.70	13	
25	4	-18 +/-	27	0.02	13	

May, 1999		DOC Flux (umoles/m ² -h)				
Station	Core	Mean	CI	r ²	n	
29A	2	59 +/-	24	0.17	15	
29A	3	103 +/-	19	0.54	14	
29A	4	24 +/-	28	0.02	15	
46	6	-239 +/-	47	0.40	17	
46	7	-96 +/-	53	0.12	14	
46	8	-85 +/-	55	0.11	13	

CI=95% confidence interval

Table 10. Dissolved Sulfide Flux from Core Incubations

April, 1998		Sulfide Flux (nmoles/m ² -h)				
Station	Core	Mean	CI	r ²	n	
25	6	752 +/-	103	0.95	7	
25	7	648 +/-	52	0.97	8	
25	8	647 +/-	71	0.95	8	
46	1	499 +/-	41	0.97	8	
46	3	638 +/-	57	0.96	8	
46	4	574 +/-	52	0.96	8	

September, 1998		Sulfide Flux (nmoles/m ² -h)				
Station	Core	Mean	CI	r ²	n	
25	1	345 +/-	40	0.94	8	
25	2	458 +/-	39	0.97	8	
25	3	480 +/-	21	0.99	8	
25	4	398 +/-	37	0.96	8	

May, 1999		Sulfide Flux (nmoles/m ² -h)				
Station	Core	Mean	CI	r ²	n	
29A	2	325 +/-	25	0.97	8	
29A	3	312 +/-	8	0.99	8	
29A	4	357 +/-	27	0.98	7	
46	6	183 +/-	40	0.81	8	
46	7	211 +/-	32	0.94	7	
46	8	181 +/-	15	0.98	7	

CI=95% confidence interval